Screen Printed Thick Film Reference Electrodes for Electrochemical Sensing

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***Abstract*— This paper presents printed thick film Ag|AgCl|KCl reference electrodes (RE) for electrochemical sensors. The screen-printed REs with 10-μm thick glass-KCl salt matrix layer exhibit a stable potential of 5 mV. Cyclic voltammetric analysis shows that the anodic and cathodic peak current of the RE increases with the scan rate in the range of 25–150 mVs^{-1}. The analytical performance of the REs shows a stable open circuit potential for the NaCl concentrations in the range of 30–100 mM. Testing the presented REs for electrochemical pH sensor application (with RuO_2-based sensitive electrode) the sensitivity of 55 mV/pH was noted in the pH range of 4.5–9. Evaluating the effect of temperature on the performance of REs, a potential variation of −3.8 mV/ °C was observed. Finally, a LabVIEW interface was developed to store, analyze, and calculate the sensitivity of the sensor under different temperature conditions. The LabVIEW interface can also be used to calculate the pH-value/temperature of unknown solutions under known temperature/pH conditions.**

***Index Terms*— Reference electrodes, pH sensor, thick film sensors, electrochemical studies, screen printing.**

I. Introduction

REFERENCE electrodes (REs) are vital to study the electrochemical changes of biological systems to both enhance understanding of these complex systems and to aid in the development of treatment for environmental or health-related issues. The electrochemical studies such as potentiometry, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) etc. require REs with a stable potential to complete an electrochemical cell [1]–[4]. Thus, REs make an important component of chemical/electrochemical sensors, which are attracting significant attention due to global push concerning environmental protection and health and safety issues in the home and workplace. As a result, innovative systems such as e-nose [5], e-tongue [6] and e-skin [1], [7] etc. are being explored.

The REs made from a range of materials ($Hg|Hg_2Cl_2$ [2], Cu|CuSO4 [8] and Hg|HgO [8], etc.) have been reported. Among these, the most commonly used REs are based on Ag/AgCl as they offer stable potential with different ionic concentrations of the solution, are easy to fabricate and are non-toxic [9]–[11]. Alternatives to traditional Ag/AgCl electrodes include Hg/HgO REs, but unfortunately, these pose environmental issues. Both thin and thick film-based Ag/AgCl REs have been used in sensing applications [4], [10], [12]. Many of these are quasi-REs, as they lack KCl layer [13], [14], which plays a crucial role in terms of stabilizing AgCl concentration [9], [15]. Due to this, in measurements such as those obtained in biological-based systems, the Ag/AgCl electrode promotes inaccuracies that lead to non- reproducible reference potential measurements [16]. Further, the conventional Ag/AgCl REs are realized on the glass, which does not go well with applications such as food quality monitoring [17], as there is a risk of broken glass fragments passing into the food. The conventional glass-based Ag/AgCl REs are also not suitable for miniaturized devices, wearable/flexible systems (due to non-flexibility of glass), and for operation in high pressure and high-temperature conditions. Screen printing has become a useful tool to overcome some of these limitations, as it allows fabrication of REs for disposable sensor on flexible substrates [18]. It also offers a simple method for obtaining thick film sensitive and reference electrode in different configurations [19], [20]. Therefore, screen printing is used in this paper to realize the new thick film REs.

The new thick film REs presented here have glass-KCl layer composition, which can be printed on different substrates including alumina and low temperature co-fired ceramics [9], [21]. The low-temperature curable binders in this printable composition enables the development of flexible and disposable REs, which can conform to curvy surfaces such as human body and thus allow reliable health-related measurements [1], [22]. Further, as thick films, the REs can be used in high-temperature applications (e.g. 25- 55°C) and for online monitoring. The work presented here is based on our presentation at 2017 IEEE Sensors Conference [23], where we reported the hydration and analytical performance of screen-printed Ag|AgCl|KCl REs. In this extended version, we present a detailed analysis of thick film RE for pH sensors and their application in water and food quality monitoring

This paper is organized as follows: The fabrication and characterization of REs are discussed in section II. The structural characterization, hydration response, analytical performance, pH sensing performance, the influence of temperature on the electrode and LabVIEW interface for online monitoring are discussed in section III. Finally, the paper is concluded in Section IV with a brief discussion about the future outlook.

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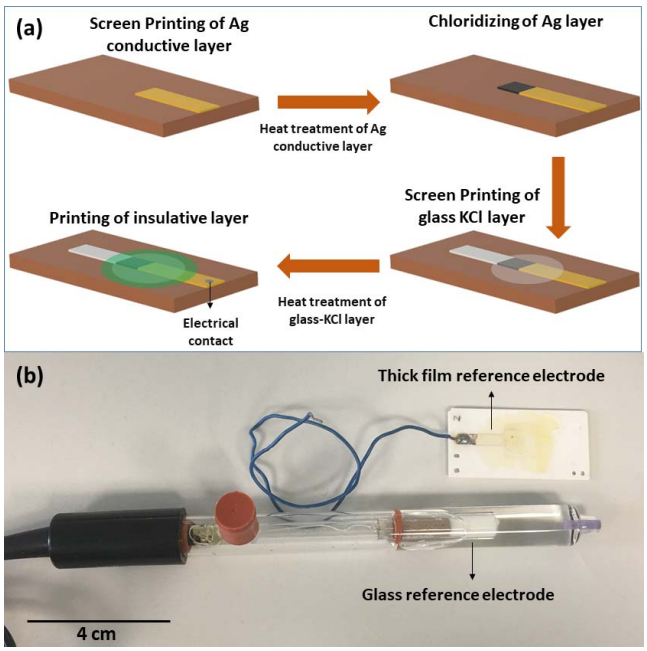

Fig. 1. (a) The fabrication steps for thick film RE. (b) Comparison of thick film and commercial glass-based RE.

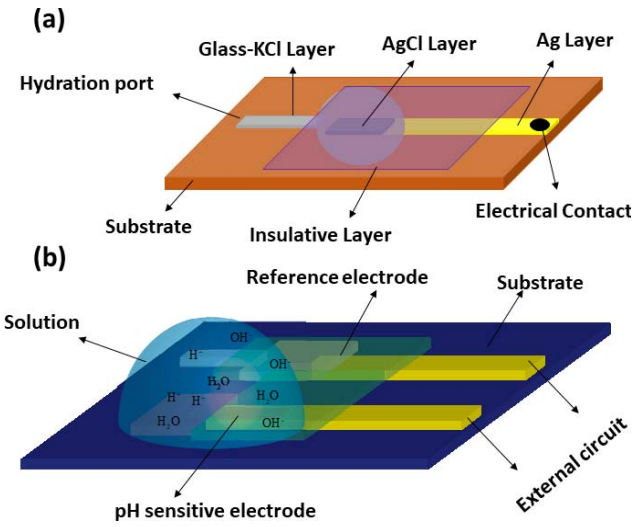

Fig. 2. (a) Three dimensional view of REs with different layers and (b) schematic representation of thick film pH sensors (both sensitive and reference electrode on same substrate) in pH solution.

II. Experimental

A. Fabrication of REs

Fig. 1a shows the schematic representation of the fabrication steps related to thick film Ag/AgCl/KCl RE. The fabrication procedure of the thick film Ag/AgCl/KCl REs is based on our previous work [9]. A lead-free glass powder-KCl composite was used to develop the KCl layer for RE. This KCl layer (salt matrix) is screen printed on top of AgCl layer. The fabricated thick film Ag/AgCl/KCl RE is much smaller in size (varied between 1.5 to 4 cm), in comparison to the commercial glass REs (10-15 cm). The thick film RE shown in Fig.1b is 4 cm in size and the glass RE has 15 cm size. To investigate the stability of potential and the hydration response, the REs with different thicknesses (~10, 20 and 30 μm) of glass-KCl film were prepared. The KCl layer plays an important role as ionic conducting path between Ag/AgCl electrode and the test solution. In this electrode configuration hydration port serves as ion transport layer as shown in Fig. 2a. The polyurethane resin-based insulation layer has been used to prevent the fast decay of glass-KCl composite on the top of Ag/AgCl layer. Fig. 2a shows the schematic diagram of fabricated RE. To evaluate the utility of REs for pH sensing application we have used the RuO_2 based sensitive electrode (SE) reported previously [9], [21]. A schematic diagram of thick film pH sensor on a single substrate fabricated by screen printing is shown in Fig. 2b. The surface morphology of glass-KCl composite layer on top of Ag/AgCl layer was investigated by using a scanning electron microscopy (FEI Nova NanoSEM).

B. Electrochemical Measurements and Characterization

All electrochemical studies were carried out by using Metrohm Autolab (PGSTAT302N, Netherland). The operation of the proposed thick film REs was investigated by measuring the open circuit potential (OCP) against commercial glass-based REs (Sigma Aldrich, UK) while dipping them in deionized water. The hydration time and the time to reach a stable potential were initially measured. The analytical performance of the thick film RE was evaluated by using cyclic voltammetry (CV) and potentiometric methods in three electrode electrochemical cell system. The CV analysis was carried out in a 3M KCl concentrated solution by varying the scan rate from 25-150 mV/s between +1 to −1V. The analytical performance of the fabricated RE and the OCP was measured against glass-based REs and the counter platinum electrode (Autolab) with different Cl^- concentration. The Cl^- ion concentration of the solution was varied by adding drops of 30-100 mM NaCl in the solution.

The performance of the developed REs under different pH conditions has been demonstrated by using them with a pH sensing electrode based on RuO_2 (the working sensitive electrode have an area of 10 mm^2). For this, the solutions with pH values 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5 and 9 were prepared by mixing diluted HCl and KOH in deionized water. A standard pH meter (HI 98130, HANNA) with temperature and conductivity probe was used to control the pH level of the solution. Initially, the potentiometric sensitivity measurements were carried out at room temperature. The Nernstian response to measure the sensitivity value is determined by the Nernst equation:

$$E = E_0 - \frac{2.303RT}{nF}pH \quad (1)$$

where E_0 is the standard potential, R is the universal gas constant, T is the temperature, F is Faraday's constant and n is number of ions. The electrochemical reaction of the sensor was also determined by using EIS analysis at pH 7. This was carried out in the frequency range of 1 mHz to 100 kHz at 10 mV applied sinusoidal signal. A complex impedance data

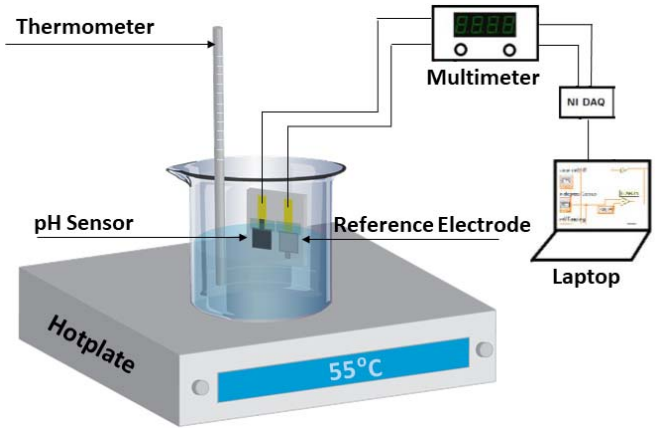

Fig. 3. The arrangement of experimental set up with temperature-regulated system connected to multimeter and interface.

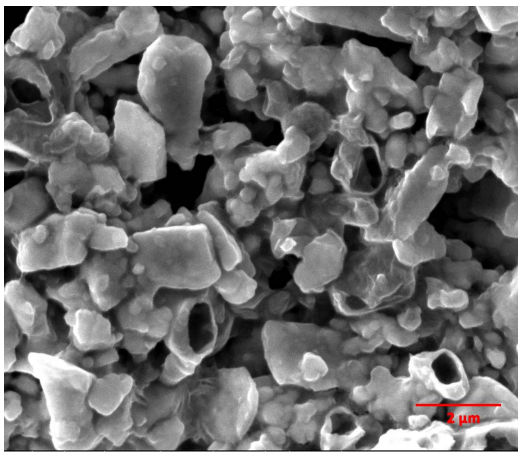

Fig. 4. SEM image of glass-KCl film.

of the obtained sensor was plotted using the Nyquist plot to predict the electrochemical reactions.

The temperature dependence of the sensing and reference electrodes were measured by varying the temperature of solution between 25- 55°C. An OCP measured against two separate REs and the sensitive electrode. A commercial glass thermometer was used to crosscheck the temperature of the solution. Fig. 3 shows the scheme of the experimental setup for above measurements. A standard buffer solution of different pH values was used for testing.

C. LabVIEW Interface Design for Data Analysis

The processing of the data is a lengthy yet essential part of measurements. For efficient processing of data, it is useful to have a system or application that can handle the data while offering a flexible user interface (UI) that can be tailored to the various aspects of the study. To address this requirement, we have also developed LabVIEW based platform. The LabVIEW includes a built-in user interface for intuitive control of the system and clear visualization of outputs. These features are similar to microcontrollers-based data acquisition solutions, but unlike the latter, they do not require external libraries for complex analysis or additional platforms to develop software interfaces.

The sensitivity of the sensor which is the focus of analysis can be calculated by the proposed LabVIEW interface through values obtained at certain temperatures and pH levels. The electrodes are dipped in a buffer solution at pH levels of 4, 6 and 8. The potentiometric readings obtained using multimeter where transferred to a computer using the data acquisition board (DAQ) from National Instruments (NI) (NI DAQ USB-6363 unit). The LabVIEW code stores and analyses the acquired data to calculate the sensitivity of the sensor. The sensitivities were calculated by the slope of the accurate best fit. In addition, the levels of pH of an unknown solution can be calculated using the Nernst equation and the data acquired and stored from these experiments. All data – input, intermediate states and output, are retained and organised within the code, should any future function of the application require them. The application developed here demonstrates LabVIEW's capabilities as an analysis tool for sensor readings. Combining compatibility with an immense range of sensors [24], [25] computer-aided computation and elimination of problematic program interfacing makes LabVIEW an exceptional package for data analysis.

For the experiments carried out in this paper, the application is currently configured to accept three primary values (pH) on the x-axis, four secondary x-axis values (temperature) and a 3x4 array of sensor potential difference measurements. The LabVIEW code is designed to graph the sensor data as dependent variable against both independent x-axis variables (i.e. pH vs Potential, Temp vs Potential) and provide a best linear fit calculation. The software then produces the sensitivity of the sensor in different temperature conditions and the E_0 value that can be deduced from the slope (i.e. mV/pH or mV/unit temperature) of the obtained fitted graph.

III. Results and Discussion

A. Morphological Characterization

The surface morphology of the glass-KCl layer on the top of AgCl film was monitored using SEM image as shown in Fig. 4. Surface morphology reveals the porous microcrystalline structure of the glass-KCl film. The rough surface and porosity of the glass-KCl layer film enable faster ionic exchange in the hydration port and to the AgCl electrode [9]. This morphology of the film enhances the sensing or electrochemical performances of the thick film RE.

B. Hydration Response and Stability Time

Prior to using the thick film RE for pH monitoring application, their hydration response was investigated by measuring the OCP with the glass RE. During initial measurement, it was noted that for freshly prepared REs the value of OCP was unstable. For example, RE with a thickness of KCl layer $\sim 10\mu$m (RE-1) the OCP was unstable for nearly 3 h. This is due to the hydration response of KCl layer. After initial stabilization, the electrodes were kept in a dry ambient and it was noted that the OCP of RE stabilized very fast. It required only a preliminary period of $\sim$ 20 min. Sometimes the KCl

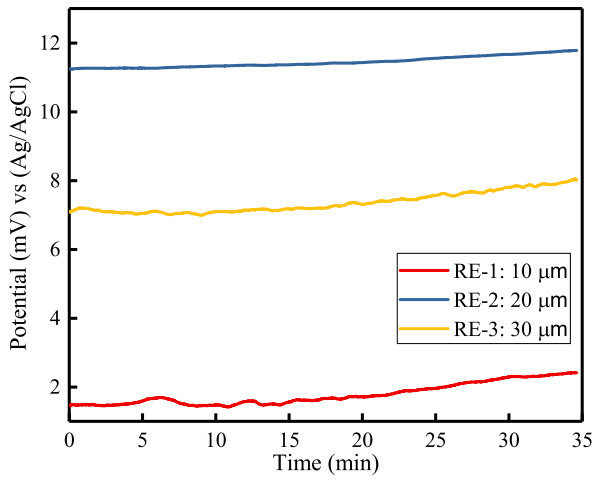

Fig. 5. Potential (emf) between the thick film RE of different KCl layer thickness with the glass RE.

layer reported in literature are deposited on the top of Ag/AgCl film. However, the thick film containing pure KCl, which easily dissolves in water, can lead to the unstable potential [15]. To overcome this issues glassy-KCl layer and polymer-KCl layer are used sometimes. As compared to the polymer-KCl matrix [26] the glassy-KCl matrix shows faster stability and this is also confirmed here. The observed hydration time (20 min, after initial stabilization) of the prepared glass KCl is comparable with the reported thick film REs [1], [4], [27]. After hydration time, the potential difference between glass and thick film REs are stable and is close to zero, as shown in Fig. 5. This implies proper operation of the fabricated thick film RE. These results reveal that for the proper functioning of ion conductive KCl channel it is necessary to keep the thick film RE in test solution after fabrication.

Fig. 5 shows the influence of glass-KCl layer thickness on the performance of RE. It can be observed that with an increase in the thickness the magnitude of measured OCP also increases. This can be due to reduced mobility of ions in the glass-KCl matrix with an increase in thickness. However, after continuous long-term measurement, the measured potential of 30 μm dropped from 11 mV to 5mV. This is due to the loss of salt matrix while reacting with a solution. The performance of thick film RE-3 (KCl with a thickness of 30 μm) measured after 2 years of storing in dry condition shows the stable potential of 5 mV against glass RE. This confirms that in the thick film REs the dimension of salt matrix layer influences the hydration response, potential and lifetime [23], [26]. The presented thick film REs show significant improvement as compared to thin film quasi-REs which show short lifetime (< 30 days) and have unstable potential due to the lack of KCl film [15].

C. Analytical Performance

The analytical performance of planar thick film RE was evaluated against glass RE by using CV analysis in 3M KCl solution with scan rate between 25-150 mV/s. From CV spectrum shown in Fig. 6a, it can be observed that the

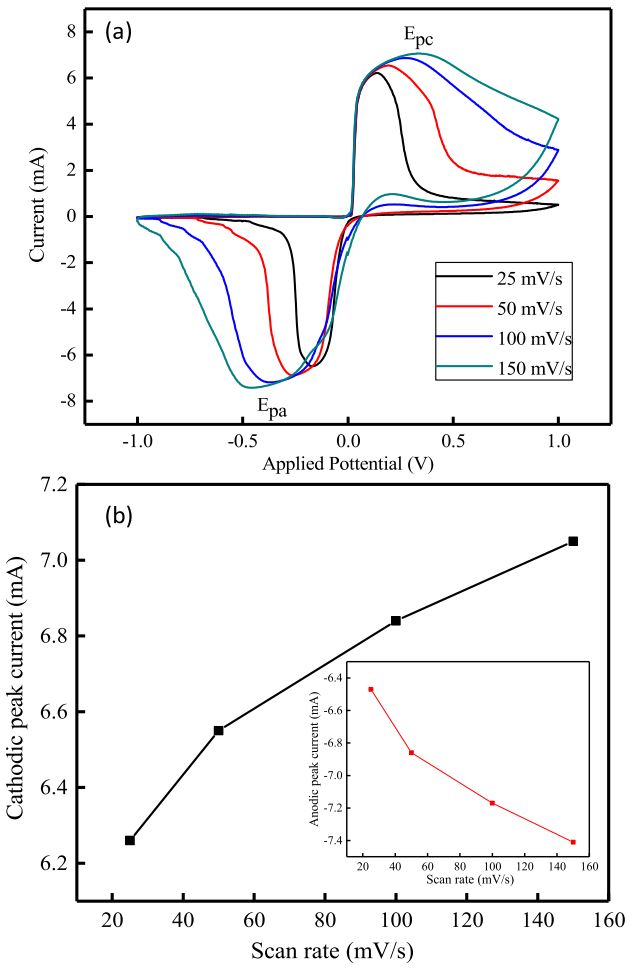

Fig. 6. (a) CV response of thick film reference electrode under different scanning rate and (b) the variation of cathodic and anodic (inset) peak current with scan rate.

potential corresponding to each scan rate shifts slightly with an increase in the scan rate. With the scan rate increasing from 25 to 150 mV/s the redox peak potential shifts from 0.14V to 0.35 V. This shift in potential is due to the quasi-reversible electron transfer reactions [28]. In these cases, the applied voltage will not generate the appropriate concentrations at the surface of electrode as it is predicted by the Nernst equation and the current takes more time to respond to the applied voltage compared to the reversible case. As the equilibria are not established fast enough compared the voltage scan rate, as a result of the slow kinetics of the reaction, the current maximum shifts depending on the reduction rate and the scan rate. In addition to this, it was found that the anodic and cathodic peak current increase with the scan rate. The variation of peak currents with scan rate is shown Fig. 6b. The increase of peak currents with scan rate (almost straight line) indicates the diffusion-controlled reaction in the electrodes.

To evaluate the performance of thick film REs towards Cl^{-}, various concentrations NaCl were mixed in a solution of pH 7. Fig. 7 shows the OCP of thick film RE for different concentration (30-100mM) of NaCl in pH 7 solution. The OCP of the electrode in each solution is almost stable after initial

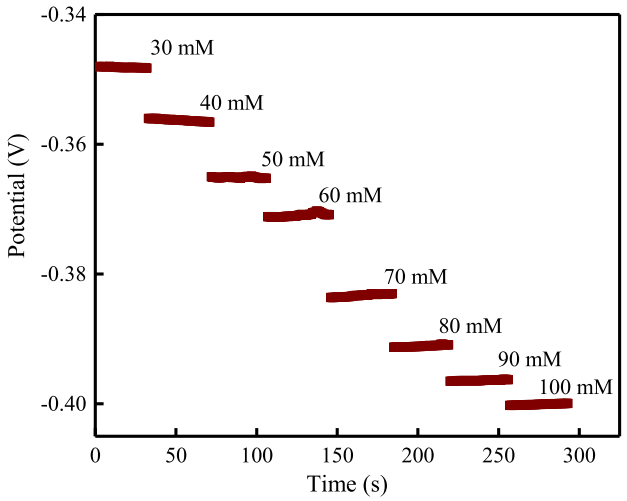

Fig. 7. Response of thick film reference electrode against a glass Ag/AgCl reference electrode in different concentration of NaCl solution.

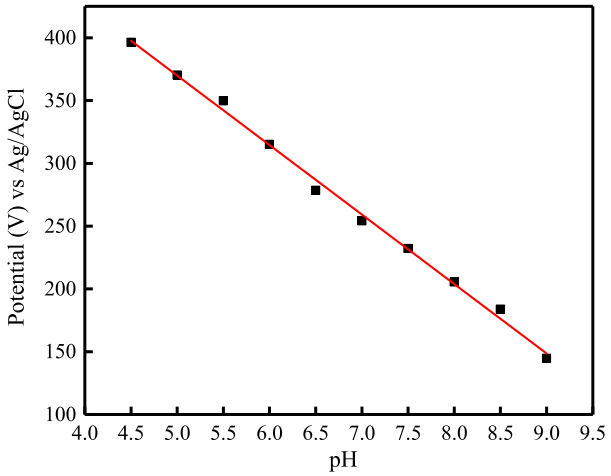

Fig. 8. Potentiometric pH sensing performance of the thick film pH sensor.

drift and varies with the concentration. These analytical performance and hydration response studies show the fabricated REs present a good alternative glass REs and that they can be used in thick film-based sensors.

D. pH Sensing Performance

One of the major applications of thick film REs is in the development of miniaturized electrochemical sensors for online monitoring. In this work, a detailed electrochemical study of two-electrode system-based pH sensor was carried out by using potentiometric and electrochemical impedance spectroscopic (EIS) methods [1], [29]. The knowledge of the OCP value between the sensitive and reference electrode in the potentiometric method will further help to determine the ionic concentration in a solution through a calibration curve. In previous works, we successfully demonstrated the pH sensing performance of the thick film RE against RuO_2 based pH-sensitive electrode [9], [21]. The sensors were fabricated on different ceramic substrates. A detailed study of this pH sensor was needed to evaluate its applications in other fields

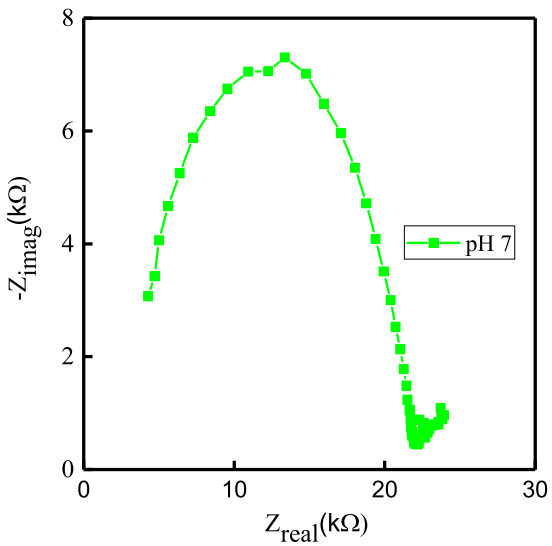

Fig. 9. Nyquist plot for two-electrode system in pH 7 solution.

such as biomedical, water and food quality monitoring. When considering the application of water quality monitoring the normal range for pH is 6 to 8.5 and for bio-application is in the range of pH 4.5 to 9. Here we tested the variation of potential with time for pH values between 4.5 to 9. The pH value of solution varied with 0.5-digit variation. We recorded the OCP in 100 s for each solution and after cleaning the sensor transferred it to the next pH solution. The Nernstian response, which represents the plot of OCP values as a function of pH, is shown in the Fig. 8. The observed Nernstian response of the fitted plot (with linear square fit $R^2 = 0.998$) from Fig. 8 is:

$$E = 646.41 - 55.31.pH \tag{2}$$

We observed that the developed thick film pH sensors show a sensitivity of 55 mV/pH in the pH range 4.5-9 with the standard potential of 646 mV. The observed sensitivity is close to ideal Nernstian response (59.12 mV/pH). A detailed evaluation of sensing mechanism and characteristics properties of the pH sensor was discussed in our previous articles using interdigitated electrodes based pH sensor [30].

To evaluate the performance of the thick film RE for electrochemical analysis we carried out the EIS analysis for the two-electrode system (reference and sensitive electrode). The complex impedance data of the sensitive and reference electrode were depicted through the Nyquist plot, shown in Fig. 9 for a pH 7 solution. The observed shape of the Nyquist plot is almost similar to the interdigitated structure based two electrode system (in high-frequency range) [30] and glass electrode based measurement [31]. The big semi-circle observed in the high-frequency range is due to the charge in transfer resistance (R_{ct}) of the material. In low-frequency range, some disturbance is observed in the impedance value, which may be due to the surface properties of the electrode. In this low frequency range (10 to 1mHz) ionic exchange prevails in the sensing reaction [29].

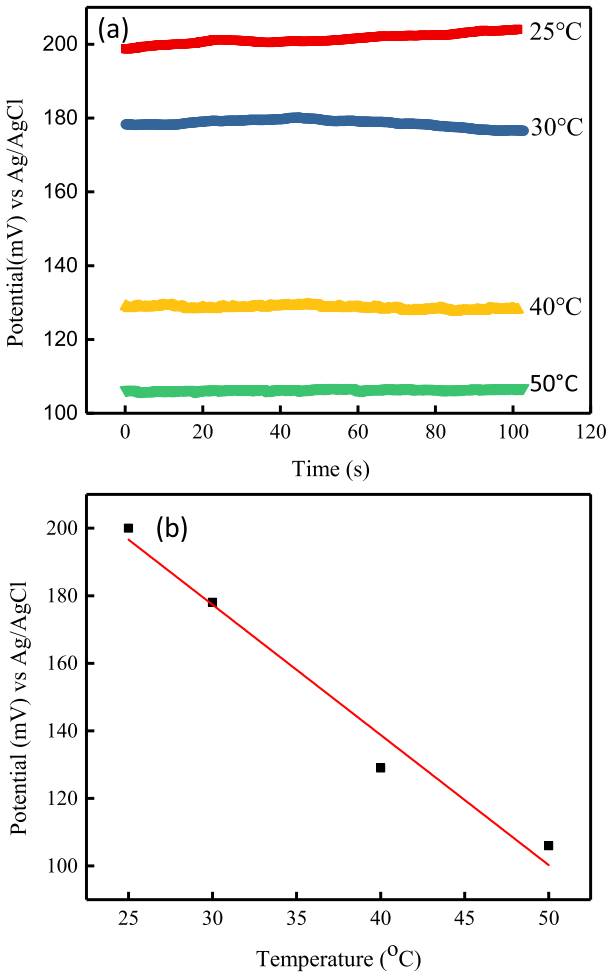

Fig. 10. (a) Stability of potential at buffer solution of pH value 5 on different temperature and (b) potential value vs temperature.

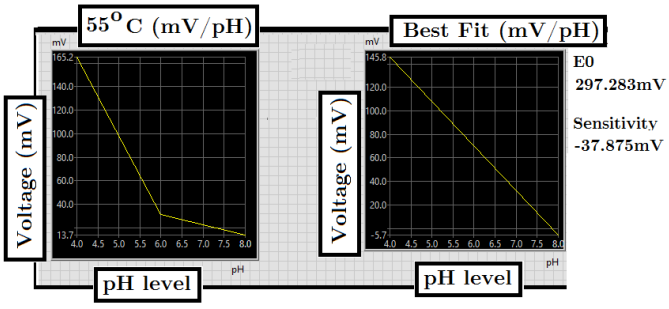

Fig. 11. Obtained and fitted graph respectively for sensor's sensitivity at 55°C.

E. Influence of Temperature

The influence of temperature on the reference and sensitive electrode potential was investigated by varying the temperature between 25°C-50°C in test buffer solution. The sensor exhibits a stable potential for each temperature value at a constant pH 6, as may be noted from the results are presented in Fig. 10a. The measured variation reveals a −3.8 mV/°C variation in the potential with temperature, as shown in Fig. 10b. The test solution contains H^+ and OH^- ions. These ions were diffused through the pores of sensitive electrode and trapped at the boundaries [32]. Here, both electrodes are based on thick film and the surface of the electrode material could influence on the variation of temperature. After keeping long period in dry atmosphere, we further tested the variation of the sensitive and reference electrode with different temperatures with varying pH values of solution using the previously discussed LabVIEW interface. We observed a variation in sensitivity of 42 mV/pH to 38 mV/pH in the temperature range of 30- 55°C, respectively Fig. 11 shows the obtained graph for sensitivity of 38 mV/pH at 55°C.

IV. Conclusion and Future Work

This work presents the analytical and electrochemical performance of a printed thick film Ag|AgCl|KCl REs. The prepared REs consist of glass-KCL film as a salt matrix layer to keep the stability of potential. The thickness of KCl layer was found to have a strong influence on REs in the initial stabilization phase (∼ 3 hr.). The fabricated planar REs with a thickness of ∼10μm shows a stable potential and close to zero against glass REs. Thick film REs exhibit stable potential in NaCl solution with concentration in the range of 30-100 mM. This implies that the planar REs have excellent analytical performance. For an electrochemical pH sensor application, the fabricated REs and sensitive electrode (RuO_2 based) show sensitivity of 55 mV pH in the range of pH 4.5 to 9. The dependence of temperature of solution on the electrodes performance reveals that the sensor exhibits a stable potential value (little variation of -3.8 mV/°C) for each temperature. Finally, the LabVIEW interface, designed for online analysis of the acquired data, was presented. Following the extensive experimental verification of planar REs, our future goal is to fabrication them on flexible substrates to meet the requirements of wearable systems.

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